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# PATENT SPECIFICATION

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## (54) DETERGENT COMPOSITIONS COMPRISING AMINE POLYPHOSPHATES

(71) We, ALBRIGHT & WILSON LIMITED, a British Company of P.O. Box. No. 3, Oldbury, Warley, West Midlands, do hereby declare the invention, for which we pray that a Patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to liquid cleaning compositions comprising a polyphosphate builder. Such compositions include both liquid detergent solutions, comprising a surface active agent such as are currently employed as dishwashing and textile detergents, and also highly alkaline solutions comprising little or no surface active agent such as are used for cleaning hard surfaces, e.g. the insides of ovens and for machine dishwashing, bottle washing, and beer keg washing. The present compositions may have various degrees of aqueous dilution and in the extreme case may be stable suspensions or gels. The polyphosphate solutions may also be dried by suitable means to provide a solid builder composition. In the gel or suspension form the compositions may be used in cosmetic detergents, e.g. shaving creams. Polyphosphate builders are useful in all such compositions both for their sequestering effect on heavy metal ions, notably calcium ions, and for their detergent builder properties additional to this sequestering effect.

Considerable efforts have been made to provide satisfactorily built cleaning compositions of the types referred to above but as yet a number of problems remain.

The primary difficulty in the case of liquid cleaning compositions arises from the varied nature of the necessary ingredients coupled with the properties which the liquid cleaning composition must possess. In the case of compositions comprising surface active agents in solution, the primary problem may be expressed as that of providing a composition, which has a sufficient concentration of surface active agents and builder in the same solution to give a satisfactory cleaning performance but which at the same time is homogeneous, has a chill point well below room temperature and a short reliquifaction time at room temperature after storage at low temperature. In addition in order to gain acceptance the solution should be sufficiently concentrated that a container of moderate size containing the solution will provide an acceptable number of washings—about as many washings as an equivalent sized container of solid detergent. All these requirements are onerous in that they increase the necessity of the builder and surface active agents having a high compatibility. Compatibility limitations are often further aggravated by the need for further ingredients such as a silicate (as a corrosion inhibitor) suds builders, and organic solvents. In the case of highly alkaline liquid cleaning compositions comprising little or no surface active agent, similar problems arise in relation to the compatibilities in aqueous solution of the phosphate builder and the alkaline ingredient which is normally a caustic alkali or a sodium silicate or a mixture of the two.

Attempts to mitigate these problems have been concentrated on varying the nature of the surface active agent and the builder so as to discover a combination having a large degree of compatibility or in incorporating a further ingredient into

the composition which is designed to homogenise the solution. Combinations of these approaches have also been used.

However, the scope for variation is limited by the desired properties of the composition and the success in alleviating the above problems has been limited.

5 The scope for varying the nature of the surface active ingredients (where used) 5  
is limited by the required detergency characteristics of the composition, that is, not  
all surface active agents possess the foaming properties (either high or low foaming  
ability may be desired), mildness washing ability and low cost which are required for  
10 use in liquid detergents. A notable difficulty arises in the case of the non-ionic sur- 10  
face active agents having the low foaming properties essential in liquid detergents for  
use in automatic dishwashing machines as well as other desirable washing properties.  
Such non-ionic surfactants may be dissolved only with difficulty in concentrated  
alkaline builder solutions unless certain specialised ingredients are added to bring  
about compatibility (see for example B.P. 991980).

15 A variety of homogenising agents designed to increase the compatibility of the 15  
various ingredients are also widely used in many types of cleaning compositions. Most  
widespread among these are the so-called "hydrotropes", notably sodium or potassium  
salts of benzene, toluene or xylene sulphonic acids and triamyl phosphate. Various  
organic copolymers have also been suggested (see for example B.P. 943353) and the  
20 incorporation of "assistant solubilizers" such as ethanol or ethylene glycol has also 20  
been proposed.

The disadvantage of all these additional ingredients is that they contribute little  
or nothing to the actual cleaning properties of the composition so that the expense  
of their incorporation must be weighed solely against their ability to enable the con-  
25 centration of the builder or surface active agent in the solution to be increased. More- 25  
over the dilution of the cleansing effect resulting from the use of such homogenizers  
lessens the effectiveness of the composition.

The third major possibility of increasing the compatibility of the ingredients of  
the compositions lies in the variation of the nature of the builder. The scope for such  
30 variation is however limited. The condensed phosphates are the most widely accepted 30  
detergent builders and many of these have been examined. The major commercially  
accepted polyphosphate builder salts are the alkali metal pyrophosphates and the alkali  
metal tripolyphosphates and the alkali metal hexametaphosphates. For liquid deter-  
gent compositions the most widely accepted builder is potassium pyrophosphate. Whilst  
35 this compound is acknowledged to be a less effective builder than other compounds 35  
such as sodium tripolyphosphate, potassium pyrophosphate is relatively free from  
the disadvantages of limited compatibility with other ingredients in detergent solu-  
tions and of hydrolysis in aqueous solutions which attach to the tripolyphosphates.  
Even so potassium pyrophosphate is not as compatible with surface active agents as  
40 might be desired and the problems outlined above still hinder the development of 40  
liquid detergents.

We have now discovered a range of cleansing compositions which considerably  
reduce the aforesaid disadvantages in comparison with the aforementioned known  
polyphosphate builders. The invention provides an aqueous cleansing composition com-  
45 prising a mixture of a plurality of polyphosphate salts of one or more primary, second- 45  
ary or tertiary amines, which mixture has been obtained by a process comprising re-  
action of an aqueous polyphosphoric acid solution comprising from 80 to 88% by  
weight of phosphorus pentoxide which has been allowed to reach equilibrium with one  
or more primary, secondary or tertiary amines without any substantial hydrolysis of  
50 the polyphosphoric acid species present in the polyphosphoric acid solution and from 50  
0.1 to 50% by weight of a water soluble surfactant.

In particular, the following advantageous properties may be listed:—

- (1) High sequestering ability for calcium and magnesium ions;
- 55 (2) Exceptionally good detergent builder properties in addition to sequestering 55  
ability;
- (3) Compatibility in aqueous solution with highly alkaline reagents and surface  
active agents substantially better than that of the conventional builder solu-  
tions;
- 60 (4) Satisfactory viscosities over a broad range of solids contents leading to con- 60  
venient handling. Such properties are desirable in the formulation of liquid  
cleansing products.

It is to be understood that whilst the mixtures are not necessarily superior to

conventional builders in all the above respects, they are nevertheless uniquely valuable in the combination of these properties which they possess.

The builder solutions are obtained by neutralisation of aqueous polyphosphoric acid solutions comprising from 80 to 88% by weight of phosphorus pentoxide. The polyphosphoric acid species present in such solutions are in equilibrium with one another and the over-all composition is governed solely by the  $P_2O_5$  content of the acid as is illustrated in the Canadian Journal of Chemistry Vol. 34 (1956) p. 790, the relevant disclosures of which are hereby incorporated by reference herein where the compositions of a number of acids which are useful according to our invention are detailed. These species are primarily the straight chain polyphosphoric acids.

Useful aqueous polyphosphoric acid solutions may be made by conventional means such as by concentration of orthophosphoric acid solutions or by dilution of polyphosphoric acid solutions having greater than the desired  $P_2O_5$  content with water. Whilst the presence of other materials in the polyphosphoric acid solutions is not excluded, it is desirable that these solutions be substantially unadulterated and polyphosphoric acid solutions derived by any of the above mentioned procedures from phosphorous pentoxide obtained by the burning of electrothermally produced phosphorus are preferred. Polyphosphoric acid solutions derived by the solution of  $P_2O_5$  in so-called "wet process" phosphoric acid, obtained by acidification of phosphate rock, are also useful according to the invention. The equilibria detailed above between the various polyphosphate acid species contained in a polyphosphoric acid having a particular  $P_2O_5$  content are set up virtually immediately in that acid, but preferably the acid is allowed to equilibrate before the neutralisation step, e.g. by allowing it to stand for a period of time at room temperature before neutralisation commences. Suitable times are from one minute upwards.

The mixtures in aqueous solution are obtained by the reaction of the polyphosphoric acid solutions with a primary, secondary or tertiary amine. Within the term 'amine' as used herein are included all compounds having an amino grouping, including cyclic amines, which are capable of neutralising phosphoric acid, i.e. all compounds having an amino grouping other than one attached to a carboxyl group, regardless of the other constituents of the molecule so that, for example, this term includes amino acids and substituted amines such as alkanolamines. Preferred amines have molecular weights below 200, most preferably below 150. Particularly valuable amines include mono-, di- and tri-ethanolamines and propanolamines. Other amines which may be used include morpholine, mono-, di- and tri-ethyl, n-propyl, iso-propyl and n-, iso- and sec-butylamines, N,N-dimethylethanolamine, aminoethylethanolamine, N-2-aminoethylethanolamine, N-methyldiethanolamine, N-methylmorpholine, N-ethylmorpholine, N,N-diethylethanolamine, N-methylethanolamine.

It may be desirable to effect the reaction step simultaneously with a dilution to bring about the desired final concentration of the builder solution, provided that such dilution does not bring about hydrolysis of the polyphosphate anion species present. It is characteristic of the builder solutions for present use that the spectrum of polyphosphate anions present, substantially corresponds to that present in the original polyphosphoric acid solution. Hydrolysis of polyphosphate anions is preferably avoided by maintaining the pH of the reaction medium in the range 4—12, preferably 6—12, most preferably 7—10 and the temperature below 70°C, preferably below 40°C, say 15°C to 70°C, or 15°C to 40°C.

Previous attempts to neutralise polyphosphoric acid solutions having a  $P_2O_5$  content in the range 80—88% by weight have failed to appreciate the necessity of avoiding the hydrolysis of the polyphosphate species during the neutralisation step. For example B.P. 919,249 describes the neutralisation of a phosphoric acid solution containing 84% by weight of  $P_2O_5$  using a mixture of diethanolamine and potassium hydroxide. The resulting polyphosphate is claimed to be a useful builder in liquid detergents; however, in order to incorporate sufficient builder in a liquid detergent solution the presence of a water miscible organic cosolvent such as ethanol is essential. The amine builder salts of our invention made under the conditions outlined above are sufficiently compatible with detergent solutions to enable the use of such an organic cosolvent to be avoided if desired. However the presence of such cosolvents in the compositions of our invention is not excluded.

In B.P. 1,066,234 there is described a solid detergent builder which is produced by the neutralisation of a polyphosphoric acid solution containing 83% by weight of  $P_2O_5$  with an excess of an alkali metal salt, preferably the carbonate. Although this patent teaches the desirability of avoiding the hydrolysis of the polyphosphate anions present it is only concerned with the alkali-metal salts and their use in admixture with alkali-metal carbonates as solid detergent builders.

The mixtures for present use are preferably those obtainable by reaction of the said phosphoric acids and the said amines in a 1:1 acid:base ratio but compounds obtainable by partial neutralisation of the polyphosphoric acids by the amines also have utility. In the general case the builders will be compounds obtainable by the reaction of the said polyphosphoric acids with the amine in a ratio of from 1:10 to 10:1, say 1:5 to 5:1, preferably 1:1 to 3:1, expressed as the ratio of amine groups to phosphorus atoms.

In any case reaction between the amine and the polyphosphoric acid mixture preferably proceeds to a final pH of from 4 to 12, preferably from 4 to 10, most preferably from 7 to 10.

The builder salts are conveniently obtained by the straightforward addition of the polyphosphoric acid to the amine or an aqueous solution thereof, followed by concentration or dilution as required for the proposed use.

In the case of the salts derived from amines which contain an hydroxy substituent on their carbon chain, it is necessary to maintain the water content of the system at a sufficient level so as to ensure the desired salt formation occurs rather than esterification such as is described in USP 3,728,419; a water level of above 15% by weight is normally sufficient. In general we prefer to maintain the water content in the builder salt solution in the range 20—40% by weight since this facilitates the handling of the product. In the case of amines which do not contain a hydroxyl group and therefore cannot be esterified, this restriction is not essential although it is preferred to maintain the water content of the system above 25% by weight. Decrease in this water content results in a progressive tendency to form a solid product and such processes are less preferred.

Solutions of the builders thus formed may provide a solid builder for incorporation into solid detergent formulations with other conventional ingredients. Preferably they are sprayed as solutions onto preformed solid detergent compositions. Such solid detergent formulations constitute a further aspect of the invention.

The mixtures may be present in the novel cleaning compositions in a wide range of concentrations depending upon the envisaged application and upon the solubility of the mixture, but in general they will be present in concentrations of from 4 to 25% by weight, more usually from 6 to 18%, e.g. from 10 to 15% by weight (all these percentages being expressed as percentages of  $P_2O_5$  from the respective polyphosphates) on the total weights of the compositions. Aqueous solutions of the polyphosphate mixtures as hereinbefore defined comprising at least 4%, preferably at least 10% thereof, on the aforesaid basis, constitute a further aspect of this invention. Preferred such solutions comprise from 6 to 18%, more specially from 10 to 16% by weight of the mixture on the aforesaid basis.

The proportion of surface active agent (where present) in the novel compositions may vary within wide limits just as with known such compositions, depending upon the use in question. In the general case, novel compositions will comprise from 0.1 to 50% by weight of surface active agent and in particular cases may comprise say from 0.1 to 5% e.g. 0.5 to 3% by weight in the case of a hard surface cleaner and from 10 to 60% by weight, say 20 to 50%, e.g. 20 to 30% in the case of a heavy duty liquid detergent. Most usually the proportion will be from 0.1 to 0.5 to 60% or 70%, more usually from 1.2, or 3% to 50, 60 or 70% by weight.

The surface active agents which may be employed in the novel compositions include non-ionic, anionic, cationic and amphoteric surface active agents, generally such as these mentioned in Volume 19, pages 507—566 of the Encyclopaedia of Chemical Technology, Second Edition by Kirk-Othmer, published by Interscience 1969, the relevant disclosure of which is hereby incorporated by reference herein.

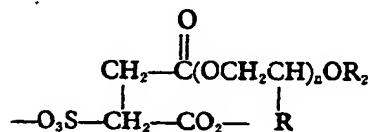
Particular surface active agents which may find use in the novel compositions include: alkyl aryl sulphonates such as lithium, sodium, potassium, ammonium or other water-soluble salts of sulphonic acids of alkyl-substituted benzenes such as decyl toluene, dodecyl-xylene, octylbenzene, nonylbenzene, decylbenzene, tridecylbenzene, tetradecylbenzene, pentadecylbenzene, dodecylbenzene and hexadecylbenzene;

olefin sulphonates such as water-soluble alkali metal and alkaline earth metal mono or di-olefin sulphonic acids comprising from 8 to 24 carbon atoms;

alkali metal or ammonium alkyl sulphates in which the alkyl groups have from 10 to 18 carbon atoms and polyoxyethylenated and polyoxypropylenated derivatives thereof;

alkali metal or ammonium salts of alkane sulphonates;

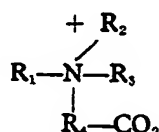
alkali metal or ammonium salts of sulphosuccinated materials of the average general formula:



wherein n is from 0 to 25, R is hydrogen or a methyl group and R<sub>2</sub> an alkyl group having from 8 to 25 carbon atoms;

amine oxides such as those described in B.P. 943,353 having the formula R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>NO, wherein R<sub>1</sub> is an alkyl radical having from 9 to 25, preferably 10 to 16 carbon atoms and R<sub>2</sub> and R<sub>3</sub> are methyl or ethyl groups;

betaines of the general formula



wherein R<sub>2</sub> and R<sub>3</sub> are alkyl or alkenyl groups containing from 1 to 6 carbon atoms and are preferably methyl groups, R<sub>4</sub> is an alkylene group containing from 1 to 6 carbon atoms and R<sub>1</sub> is an alkyl or alkenyl group containing from 8 to 18 carbon atoms;

amido-amine derivatives having the formula



where R represents an alkyl or alkenyl group having from 8 to 20 carbon atoms, R<sub>1</sub> and R<sub>2</sub> are the same or different groups selected from hydrogen atoms, methyl or ethyl groups and n is an integer in the range 1 to 4.

polyoxethylene compounds of the general formula RO(CH<sub>2</sub>CHR'O)<sub>x</sub>H where R is an alkyl, aryl, alkaryl, alicyclic, acyl, amino or alkylamino group; R' is hydrogen or an alkyl group having from 1 to 4 carbon atoms and x is from 3 to 100, usually from 6 to 50. Such compounds include fatty alcohol polyethoxylates, fatty acid polyethoxylates, polyethylene glycol ethers, mixed polyethylene and polypropylene glycol ethers, amine and diamine polyethoxylates, and fatty alkylolamide ethoxylates;

fatty alcohol phosphates and polyethoxylated and polypropyloxyated derivatives thereof;

fatty acid soaps.

The novel compositions comprising surface active agents will normally be compounded by addition of an aqueous solution of the surface active agent (or agents) used to a solution of the polyphosphate mixture, optionally followed by dilution, although other means may also be used.

The novel compositions may also comprise known adjuvants for liquid cleaning compositions such as anti-soil redeposition agents, e.g. carboxymethyl cellulose, polyvinyl pyrrolidone, or the sodium salts of a 1:1 copolymer of di-isobutylene and maleic anhydride, optical brightening agents; perfumes; dyes; bacteriostats and bacteriocides; opacifying agents; colorants; sudsing agents, e.g. ethanolamides such as coconut ethanolamide and fatty alcohols such as lauryl alcohols; phase stabilisers such as aliphatic alcohols and homogenizing agents. Although the polyphosphate builders generally permit less homogenizing agent to be present than would be necessary with conventional phosphate builders, the preferred compositions of the invention are those which include a so-called hydrotrope such as an alkali metal, alkaline earth metal or ammonium salt of benzene-, naphthalene, an alkylbenzene- or an alkyl naphthalene-sulphonic acid having not more than 5 aliphatic carbon atoms. Preferred such hydrotopes are sodium xylene sulphonates (sold by Albright and Wilson Limited under the registered trade name 'Eltesol'), sodium toluene sulphonate, sodium benzene sulphonate and sodium naphthalene sulphonate. Preferably hydrotopes are present in the novel compositions in proportions of from 2 to 20% by weight, more preferably 2 to 10%.

most preferably 3 to 5%. In the case of hard surface cleaners of the invention, it may also be desired to incorporate a chlorine-releasing agent which is preferably sodium hypochlorite although chlorinated isocyanurates can also be used. Normally, chlorine-releasing agents, where used, will be present in a concentration such as to give from 0.5 to 3%, e.g. 1 to 2% available chlorine (w/v).

Compositions of the invention may be employed to advantage in a range of cleaning applications such as the cleaning of textiles, including wool, wood, leather, metal, earthenware, china and stone as well as for human use.

The polyphosphate builders of the invention are particularly applicable in liquid detergent compositions designed for the cleaning of fine fabrics. These compositions will normally contain from 4 to 10% of the polyphosphate, expressed as the weight of  $P_2O_5$  and from 0.1 to 5% by weight of a suitable surfactant which is preferably a non-ionic surfactant.

The invention is illustrated by the following examples in which all parts are expressed on a weight basis and all proportions of proprietary surfactant ingredients are expressed in terms of active ingredient (a.i.), any water present in the surfactant as added being included in the given proportions of total water.

#### Example 1

A composition was made up as follows:

Monoethanolamine polyphosphate comprising 36.75% by weight $P_2O_5$ and 63.25% by weight Monoethanolamine	8% expressed $P_2O_5$
1 Nansa SS 60	15%
2 Empimin KSN 27	8%
Lauric/myristic monoethanolamide	2%
3 Eltesol SX 93	3.7% a.i.
Water	to 100%

- (1) Registered trade name for a 60% w/w aqueous paste of sodium dodecylbenzene sulphonate supplied by Albright & Wilson Ltd.
- (2) Registered trade name for a 27% aqueous solution of ethoxylated sodium lauryl sulphate comprising three ethylene oxide groups per molecule supplied by Albright & Wilson Ltd.
- (3) Registered trade name for a 93% sodium xylene sulphonate supplied by Albright & Wilson Ltd., the balance of the material being sodium sulphate and water.

The product was suitable for use as a dishwashing detergent for manual use, being a clear homogeneous liquid at ambient temperature. By contrast the same formulation wherein the monoethanolamine polyphosphate was replaced by tetrapotassium pyrophosphate at a level of 8% as  $P_2O_5$  separated into two phases.

#### Example 2

A composition was made up having the same composition as that of Example 1 save that it contained 12% (expressed  $P_2O_5$ ) monoethanolamine polyphosphate and 4.7% Eltesol SX 93. Again, the composition was a clear homogeneous liquid at room temperature suitable for use as a dishwashing detergent.

By contrast, the same composition with sodium tripolyphosphate substituted at equivalent  $P_2O_5$  content for the monoethanolamine polyphosphate separated into two distinct phases at room temperature. The same result was obtained when potassium pyrophosphate was likewise substituted for the monoethanolamine polyphosphate.

#### Example 3

A composition was made up as follows:

Monoethanolamine polyphosphate	16.8% (expressed as $P_2O_5$ )
Nansa SS 60	15% a.i.
Lauric/myristic monoethanolamide	2%
Eltesol SX 93	3.7% a.i.
Water to	100%

This composition was again a clear homogeneous liquid at room temperature suitable for use as a dishwashing detergent.

By contrast, replacement of the monoethanolamine polyphosphate by 16.8% (expressed as  $P_2O_5$ ) of potassium pyrophosphate gave a composition which subsisted as two phases at ambient temperature.

#### Example 4

5 A composition was made up as follows: 5

	Isopropanolamine polyphosphate comprising	
	31—82% by weight $P_2O_5$ and 68.18%	
	by weight isopropanolamine	12.6% (expressed as $P_2O_5$ )
	Nansa SS 60	12% a.i.
10	(1) Empimin KSN 60	6% a.i.
	Lauric/myristic monoethanolamide	2%
	Eltesol SX 93	2.8%
	Water to	100%

15 (1) Registered trade name for a sodium lauryl ethoxy sulphate comprising 3  
ethylene oxide groups per molecule in 60% aqueous solution comprising 10%  
ethanol as solubiliser supplied by Albright & Wilson Ltd. 15

20 The composition was a clear, homogeneous liquid at ambient temperature, suitable for use as a dishwashing detergent. As in previous examples, replacement of the  
isopropanolamine polyphosphate by an equivalent amount of potassium pyrophosphate  
expressed at  $P_2O_5$ , gave a two-phase composition at ambient temperature. 20

#### Example 5

A composition was made up as follows:

	(1) Nansa SSA	3% a.i.	
	Triethanolamine	2%	
25	Monoethanolamine	1.5%	25
	Coconut fatty acid	8%	
	Monoethanolamine polyphosphate as		
	used in Example 1	9.6% (expressed as $P_2O_5$ )	
	(2) Eltesol PCS 93	5% a.i.	
30	(3) Empilan KA 5	5% a.i.	30
	Water to	100%	

(1) Registered trade name for a ca. 96% dodecylbenzene sulphonic acid supplied  
by Albright & Wilson Ltd.  
35 (2) Registered trade name for a 93% potassium cumene sulphonate the balance  
being potassium sulphate and water, supplied by Albright & Wilson Ltd. 35  
(3) Registered trade name for lauryl alcohol ethoxylate comprising approximately  
60% by weight ethylene oxide supplied by Albright & Wilson Ltd.

40 This composition was a clear, homogeneous liquid at ambient temperature and  
was suitable for use as a heavy duty liquid detergent for mechanical washing appli-  
ances. 40

By contrast, replacement of the monoethanolamine polyphosphate by an equivalent  
quantity of potassium pyrophosphate gave a two-phase composition at ambient tem-  
perature.

#### Example 6

45 A composition was made up as follows: 45

	Monoethanolamine polyphosphate as	
	used in Example 1	12% (expressed as $P_2O_5$ )
	(1) Empilan PPE 2910	1% a.i.
	Coconut fatty acid	2%
50	Triethanolamine	0.4%
	Eltesol PCS 93	5% a.i.
	Water to	100%

(1) Registered trade name for a high molecular weight polycondensate of pro-  
pylene and ethylene oxides supplied by Albright & Wilson Ltd.

The composition was a clear, homogeneous solution for use as a dishwashing detergent for mechanical washing. Replacement of the monoethanolamine polyphosphate by an equivalent amount of potassium pyrophosphate gave a composition which was a thick paste at ambient temperature.

5

## Example 7

5

Two compositions were made up as follows:

## Composition 1

	Monoethanolamine polyphosphate as used in Example 1	12% (expressed as $P_2O_5$ )	
10	30% aqueous solution of ethoxylated potassium lauryl phosphate comprising 5 ethylene oxide groups per molecule and consisting essentially of a 1:1 per molar mixture of mono (laurylpent-ethoxy) phosphate and di (laurylpent-ethoxy) phosphate		10
15	Water to	3.6% a.i. 100%	15

## Composition 2

20	As (1) but with isopropanolamine polyphosphate (as used in Example 4) replacing monoethanolamine polyphosphate.		20
	Both compositions (1) and (2) were clear, homogeneous liquids at ambient temperature, suitable for use as liquid detergents for hard surface cleaning.		
25	By contrast, a composition wherein 12% (expressed as $P_2O_5$ ) of potassium pyrophosphate replaced the monoethanolamine (or isopropanolamine) polyphosphate separated into two distinct phases at ambient temperature.		25

## Example 8

A composition was made up as follows:

	Monoethanolamine polyphosphate as used in Example 1	4% (expressed as $P_2O_5$ )	
30	+Empicol LQ 33	10% a.i.	30
	-Empigen BB	2% a.i.	
	Eltesol SX 93	2%	
	Water to	100%	
35	+ Registered trade name for a 33% aqueous solution of monoethanolamine lauryl/myristyl sulphate supplied by Albright & Wilson Ltd.		35
	- Registered trade name for a 30% aqueous solution of alkyl dimethyl betaine represented by the formula $R-N^+-Me_2CH_2CO_2^-$ where R is predominately lauryl/myristyl supplied by Albright & Wilson Ltd.		

The composition was a clear homogeneous liquid at ambient temperature suitable for use as a liquid hand cleanser.

By contrast a composition where potassium pyrophosphate replaced monoethanolamine polyphosphate at 4%  $P_2O_5$  level was a heterogeneous paste at ambient temperature.



## Example 9

A composition (1) found highly suitable for both machine and hand washing of woollen garments was made up as follows:

5	Nansa SSA	10% a.i.	
	Triethanolamine	6%	5
	Monoethanolamine	3%	
	+Empimin KSN 27	2.7%	
	Coconut fatty acid	4%	
10	Monoethanolamine polyphosphate as used in Example 1	6% (expressed as $P_2O_5$ )	10
	Empilan PPE 2910	2% a.i.	
	Optical brightening agent	0.2%	
	Bactericide	0.1%	
15	Perfume	0.2%	
	Water	to 100%	15

+ Registered trade name for a 40% aqueous solution of a disodium alkylethoxy sulphosuccinate halfester where the alkyl group are predominately lauryl/myristyl and the ethoxy group is primarily derived from diethylene glycol (supplied by Albright & Wilson).

20 A further composition (2) of similar utility was also made to the same formulation save that 2% of Triton CF32 replaced the Empilan PPE 2910 (Triton CF32 is a registered trade name for a non-ionic surface active amine polyglycol condensate supplied by the Rohm & Haas Company).

A composition (3) was also made up as follows:

25	Nansa SSA	10% a.i.	25
	Triethanolamine	4.4%	
	Monoethanolamine	2.2%	
	Empicol SDD	4%	
30	Isopropanolamine polyphosphate as used in Example 4	6% (expressed as $P_2O_5$ )	30
	Optical brightening agent	0.3%	
	Bactericide	0.1%	
	Perfume	0.1%	
	Water	to 100%	

35 Compositions 1 and 2 were of the 'low-foam' type incorporating coconut fatty acid soap with either Empilan PPE 2910 or Triton CF 32 as foam depressants. All three compositions (1), (2) and (3) were clear homogeneous liquids at room temperature.

Each of these compositions was compared in standard washing tests to a typical conventional detergent powder of the following compositions:

40	Sodium dodecylbenzene sulphonate	9%	40
	Fatty alcohol polyethoxylate (II mols. $Et_2O$ )	4%	
	Sodium silicate 1:2	5%	
	Sodium tripolyphosphate	42%	
	Optical brightening agent	0.49%	
45	+Alcalase P	0.5%	45
	Perfume	0.2%	
	Moisture	10%	
	pH (1% solution) ca. 10		

+ a proteolytic enzyme supplied by Novo Industria SA

50 The effectiveness of compositions 1, 2 and 3 and of the reference powder was then determined in duplicate standard washing tests. These involved subjecting 40 3" by 3" swatches of a standard test cloth to the rotating washing action of a launder-O-meter supplied by the Atlas Electrical Device Co. (Chicago). Swatches were washed in pairs (two swatches per cylinder of the loading table) with the addition of 2 g of the composition under test to each cylinder. Washing was at 80°C using water of given hardness, proceeding for 20 minutes following which the swatches were rinsed, ironed dry between cotton cloths and then compared for light reflectance using Harrison

colour measurements with a white tile reference and a light source filtered through a green filter. Results are quoted as percentages calculated from the equation:

$$\% = \frac{100 \times (\text{Reflectance A (washed)} - \text{Reflectance A (unwashed)})}{(\text{Reflectance R (washed)} - \text{Reflectance R (unwashed)})}$$

Where reflectance A is the colour scale reading of the swatch washed in the composition under test and reflectance R is the colour scale reading of the swatch washed in the reference composition.

One series of tests was carried out using standard soiled wool swatches reference Empa 102 (supplied by Empa Laboratories, Switzerland) using both water of hardness 50 ppm (CaCO<sub>3</sub>) and water of 300 ppm (CaCO<sub>3</sub>) hardness—the atomic ratio of Ca:Mg present in the water being 4:1 in both cases. Results were as follows:

	Soft Water (%)	Hard Water (%)
Reference Powder	100	100
Composition 1	92.6	86.8
Composition 2	87.6	86.8
Composition 3	95.0	90.0

These results are within the range for a liquid detergent compared with a powder and compare favourably with results obtainable from conventional liquid detergents as is demonstrated below.

Similar tests were also carried out using soiled polyester/cotton swatches (60/40 Dacron/cotton) supplied by Test Fabrics Inc. with the following results:

	Soft Water (%)	Hard Water (%)
Reference Powder	100	100
Composition 1	89.3	118
Composition 2	75.0	122.7
Composition 3	93.8	124

Here it may be seen that the performances of compositions of the invention actually surpass that of the reference powder under the most testing washing conditions, that is in hard water.

Washing colour stability tests were also carried out on compositions 1, 2 and 3 according to I.W.S. method number 105 using standard dyed woollen fabrics. Assessment of colour change and staining were carried out on the British Standards Institute Grey Scale, the preferred total being 27 points minimum.

Results were:

Reference Powder	23.5 Points
Composition 1	30.5 Points
Composition 2	30.5 Points
Composition 3	32.0 Points

To further demonstrate the improved effectiveness of the compositions of the invention, their performance was compared with that of similar compositions made up using conventional polyphosphate molecules at approximately the highest concentration possible without causing cloudiness or precipitation or phase separation at lower temperatures (i.e. the highest concentration possible for a commercially acceptable composition). These conventional formulations (A, B, C and D) were as follows:

A. Nansa SS 60	10.0%
Empimin KNS 27	10.0%
Tetrapotassium pyrophosphate	6.5% (expressed as P <sub>2</sub> O <sub>5</sub> )
+Empilan CDE	2.5%
Eltesol SX 93	9.0%
Optical brightening agent	0.2%
Bactericide	0.1%
Water	to 100%

+ Registered trade name for a surfactant active diethanolamide derivative of "total" coconut fatty acid supplied by Albright & Wilson Ltd.

	B.	Nansa SS 60	8.5%		
		+Empicol ESB 3	13.0%		
		Empilan CDE	1.0%		
5		Tetrapotassium pyrophosphate	5.0% (expressed as P <sub>2</sub> O <sub>5</sub> )		
		Elteson SX 93	5.0%	5	
		Optical brightening agent	0.2%		
		Bactericide	0.1%		
		Perfume	0.2%		
		Water	to 100%		
10	+	Registered trade name for a 27.5% aqueous solution of sodium lauryl ethoxy sulphate comprising two ethylene oxide groups per molecule.			10
	C.	Triethanolamine dodecylbenzene sulphonate	14% a.i.		
		Empimin KSN 27	4.0%		
15		Tetrapotassium pyrophosphate	6.5% (expressed as P <sub>2</sub> O <sub>5</sub> )		
		Coconut fatty acid soap	5.0%	15	
		Triton CF 32	4.0%		
		=Eltesol SCS 93	2.0%		
		Optical brightening agent	0.2%		
		Bactericide	0.1%		
20		Perfume	0.2%		
		Water	to 100%	20	
	=	Registered trade name for a 93% sodium cumene sulphonate the balance being sodium sulphate and water—supplied by Albright & Wilson Ltd.			
25	D.	Empilan KA 5	10%		
		Empimin KSN 27	1.35%		
		Tetrapotassium pyrophosphate	3.5% (expressed as P <sub>2</sub> O <sub>5</sub> )	25	
		Eltesol SX 93	5%		
		Optical brightening agent	0.2%		
		Bactericide	0.1%		
30		Perfume	0.2%		
		Water	to 100%	30	

And the washing performance of these compositions A—D was compared with those of the above compositions 1 and 2 by the method as before against the same reference powder, Standard wool swatches (Empa 102) were used.

Results were as follows (quoted in the same basis as before):

Composition	Soft Water (%)	Hard Water (%)
Reference Powder	100	100
1	87	89.5
2	87	89.0
A	85	82
B	85	48.0
C	—	62.0
D	85.5	56

The improved detergent performance of the compositions 1 and 2 of the invention is clear from these results. This is especially evident in the tests using hard water where the sequestering ability of the polyphosphate builder is most critical.

A particularly striking comparison is that between the effect of composition C and those of 1 and 2. Although the latter contain less Empimin KSN 27 active ingredient, less coconut fatty acid, less non-ionic surfactant and less "hydrotrope" (Eltesol SCS 93) they nevertheless exhibit improved detergent properties in hard water ascribable to the superior building properties of the polyphosphate builders of the invention over the conventional tetrapotassium pyrophosphate.

#### Example 10

572 Kilograms of an aqueous solution of a phosphoric acid containing 84% by weight of phosphorus pentoxide representing 32.2 parts by weight of the reaction

mixture were added to a solution of 37.9 parts of monoethanolamine in 29.9 parts by weight of water in a jacketed stainless steel vessel equipped with a turbin mixer over a period of 2½ hours with efficient cooling and stirring. The temperature was held below 40°C throughout. The product monoethanolamine polyphosphate was a straw coloured viscous liquid comprising 27.0% by weight of  $P_2O_5$  having a viscosity of 1500 centistokes at 20°C and a density of 1.375. The product was useful according to the Examples.

#### Example 11

To 443 g isopropanol amine in 297 g water was added slowly, with stirring, at between 15 and 40°C 260 g of a polyphosphoric acid solution comprising 85% by weight  $P_2O_5$ . The pH was between 4 and 10 throughout. The product was suitable for use according to Example No. 4.

#### Example 12

Isopropanolamine polyphosphate was prepared by an analogous procedure to that used in Example 10 using 24.65 parts of a polyphosphoric acid containing 84% by weight of phosphorus pentoxide, 44.3 parts of monoisopropanolamine and 31.05 parts of water. The product was a clear viscous liquid useful according to Example 4.

#### Example 13

A composition was made up as follows:

20	Monoethanolamine polyphosphate (as used in Example 1)	9.6% as $P_2O_5$	20
	Empilan 2910	3%	
	Ethylene diamine tetra-acetic acid	0.2%	
	Phosphoric acid	2.6%	
25	Potassium hydroxide (50%)	9.1%	25
	Sodium metasilicate pentahydrate	5.0%	
	Formalin (40% solution)	0.2%	
	+ Acrysol ASE 108	6.25%	
	Water	to 100%	

30 + Acrysol ASE 108 is a registered trademark for a high molecular weight acid copolymer emulsion supplied by the Rohm & Haas Company.

The product was a homogeneous liquid highly suitable for use in mechanical dishwashers.

#### WHAT WE CLAIM IS:—

- 35 1. An aqueous cleaning composition which comprises from 4 to 25% by weight expressed as the weight of  $P_2O_5$  on the total weight of the composition of a mixture of a plurality of polyphosphate salts of one or more primary, secondary or tertiary amines which mixture has been obtained by forming an aqueous polyphosphoric acid solution comprising from 80 to 88% by weight of phosphorus pentoxide which has been allowed to reach equilibrium and subsequently reacting the said polyphosphoric acid solution with a primary, secondary or tertiary amine without causing any substantial hydrolysis of the polyphosphate species present in the acid; and from 0.1 to 50% by weight of a water soluble surfactant.
- 40 2. A composition according to claim 1 wherein the surfactant is anionic.
- 45 3. A composition according to claim 2 wherein the surfactant is an alkyl aryl sulphionate.
4. A composition according to claim 1 wherein the aqueous polyphosphoric acid solution comprises from 82 to 86% by weight of  $P_2O_5$ .
- 50 5. A composition according to any of the preceding claims wherein the reaction between the polyphosphoric acid and the amine takes place at a pH of from 4 to 12 and at a temperature of from 15 to 70°C and in the case of hydroxy substituted amines the water content of the reaction system is maintained at above 15% by weight of the reaction mixture.
- 55 6. A composition according to claim 5 wherein the amine has a molecular weight of less than 200.
7. A composition according to claim 6 wherein the amine is a mono, di or tri ethanolamine or propanolamine.
8. A composition according to any of the preceding claims wherein the polyphosphoric acid is reacted with the amine in a molar ratio of from 1:1 to 3:1.

9. A composition according to any of the preceding claims which comprises a mono, di or tri ethanolamine salt of an alkyl benzene sulphonic acid.

10. A composition according to any of the preceding claims which comprises from 6 to 18% by weight (expressed as weight of  $P_2O_5$  on the total weight of the composition) of the mixture of polyphosphates.

11. A composition according to any of the preceding claims substantially as described with reference to the foregoing examples.

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